Mechanistic insights into pH-dependent hydrogen 

electrocatalysis by flipping interfacial water

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Abstract. A grand challenge in electrochemistry is to understand and promote electrochemical processes by exploring and exploiting the interface. Herein, we promoted the hydrogen evolution and oxidation reactions (HER/HOR) of platinum in base by employing N-methylimidazoles to reorientate interfacial water against the interfacial electric field as evidenced by in situ spectroscopic characterization of the interface. We accordingly established a unified mechanism by which the HER/HOR in acid and base proceeds via diffusion of proton and hydroxide, respectively, through interface via interfacial water by the Grotthuss mechanism. This mechanism accounts for the pH-dependent HER/HOR kinetics of platinum, a long-standing puzzle. Furthermore, we demonstrated 40% performance improvement of an anion exchange membrane electrolyzer by adding 1,2-dimethylimidazole into the alkaline solution fed into its Pt cathode.
The pH has profound influences on the kinetics of electrochemical reactions such as hydrogen electrocatalysis. The hydrogen evolution and oxidation reactions (HER/HOR) activity of several transition metals like platinum (Pt) progressively slows down as the pH increases (1-3). The reason(s) behind this phenomenon has remained unclear despite decades of studies. One primary strategy adopted in these studies is to mix Pt with another metal such as Ni or Ru to improve its HER/HOR activity in alkaline media, followed by identification of the promoting roles of Ni/Ru (4-10). However, different groups proposed different promoting roles of Ni/Ru and accordingly suggested different causes of the sluggish HER/HOR of Pt in base. Some groups stated that the Ru/Ni improves the HER/HOR of Pt by weakening the binding energy of Pt and hydrogen ($E_{PtH}$) via strain and/or electronic effects, and ascribed the sluggish HER/HOR of Pt in base to the overly strong $E_{PtH}$ (8-11). Other groups proposed that Ru/Ni promotes water dissociation/formation owing to its high oxophilicity, and attributed the sluggish HER/HOR of Pt in base to the high energy barriers of water dissociation/formation (4, 6, 7). Koper’s and Feliu’s groups showed that the Ni deposited on Pt surfaces negatively shifts the potential of zero free charge (pzfc, the potential where the excess of electrons in the metal is zero), which eases the flip of interfacial water and in turn promotes the HER/HOR of Pt in alkaline solution (12-14). They accordingly attributed the pH-dependence of the HER/HOR activity of Pt to the pH-dependent pzfc, which has lately come under scrutiny (15, 16). We recently identified the promoting role of Ru as facilitating interfacial water shuffling of the HER/HOR intermediates (17) and postulated that the stiffening of interfacial water by the negatively charged Pt surfaces determines the sluggish HER/HOR of Pt in base. Because of the ambiguity over the promoting roles of Ni/Ru, this strategy has not led to a verdict of the sluggish HER/HOR kinetics of Pt in
base. Finding other types of promoters with definitive promoting roles may give definitive answers to this open question and provide new routes to promote the HER/HOR of Pt in base.

Most recently, Snyder’s group (18) found that adding caffeine into alkaline solution substantially improved the HER/HOR activity of Pt in base, but the improvement mechanism was unclear. This work inspired us to seek other organic compounds that promote the HER/HOR of Pt in alkaline solution and then identify their promoting roles to understand the sluggish HER/HOR kinetics of Pt. By studying a set of N-methylimidazoles via a combination of rotating disk electrode (RDE), $^{14}$N/$^{15}$N nuclear magnetic resonance (NMR), and density functional theory (DFT), we found that the N-methylimidazole with a more negatively charged pyridinic nitrogen (N$_3$) bound the H of interfacial H$_2$O stronger and improved the HER/HOR activity of Pt more. In situ attenuated total reflectance surface-enhanced infrared reflection absorption spectroscopy (ATR-SEIRAS) coupled with in situ surface-enhanced Raman further showed that 1,2-dimethylimidazole stabilized the interfacial H$_2$O with the H-up configuration ($\uparrow$H$_2$O) via the N$_3$···$\uparrow$H$_2$O bonding. These findings enabled us to pinpoint the promoting role of N-methylimidazoles as stabilization of interfacial $\uparrow$H$_2$O to catalyze the proton-coupled electron transfer (PCET) process and concluded that the slow HER/HOR kinetics of Pt in base is due to destabilization of interfacial $\uparrow$H$_2$O by the repelling interfacial electric field (IEF).

We first verified that adding $10^{-5}$ M caffeine into 0.1 M KOH electrolyte markedly improved the HER/HOR activity of Pt/C (TKK, 47.7 wt%) (Fig. S1A) in a RDE as originally reported by Snyder and co-workers (18). We then tested $10^{-5}$ M 1,3-dimethyluracil and 1-methylimidazole, the left and right parts of caffeine, respectively, to specify which part(s) of caffeine contribute to the improvement. The 1,3-dimethyluracil did not promote the HER/HOR of Pt (Fig. S1B), whereas 1-methylimidazole did (Fig. S1C). Driven by this finding, we tested a
set of N-methylimidazoles with different numbers of methyl groups (-CH₃) located at different positions of the imidazole ring (Fig. 1), which allows for tailoring the structure of these HER/HOR promoters at the molecular scale. These compounds are accordingly labelled by the locations of methyl groups hereafter (for example, Me-C₄ for 4-methylimidazole and Me-N₁C₂ for 1,2-dimethylimidazole). We quantified their improvements of the HER/HOR specific exchange current densities (i₀) of Pt/C by fitting the kinetic currents to the Butler–Volmer equation (the HER/HOR curves are present in Fig. S2) (19). The electrochemical surface area (ECSA) was derived from the hydrogen underpotential deposition (H_upd) charge of the cyclic voltammetry (CV) of Pt/C in 0.1 M KOH within the potential range of 0.05-0.45 V (all potentials here are versus reversible hydrogen electrode (RHE)). The average i₀ of Pt/C in these cases is 0.64±0.02 mA·cm⁻², comparable to that (0.57±0.07 mA·cm⁻²) of Pt/C reported previously (20) under similar conditions. Although the H_upd charge of Pt/C was significantly suppressed by adding the N-methylimidazoles (Fig. S3), the HOR limiting current density remained unchanged for all cases. These phenomena indicated that these N-methylimidazoles did not block the Pt sites for the HER/HOR. We therefore used the H_upd charge of Pt/C obtained in the 0.1 M KOH electrolyte prior to addition of N-methylimidazoles as the ECSA of the Pt/C in 0.1 M KOH with N-methylimidazoles.
Fig. 1. N-methylimidazoles promote the HOR/HER of Pt through the N₃⋯H₂O bonding.

The $i_0$ improvements (red dots, left y-axis) and the $^{14}$N₃/$^{15}$N₃ chemical shift changes (blue squares, right y-axis) of N-methylimidazoles between two different medias as a function of the charge of their N₃(s). The charges of the N₃ were determined by DFT, with the rapid averaging of the N₁ and N₃ charge via proton exchange (21) taken under consideration for imidazole, Me-C₂, Me-C₄, and Me-C₂,₄ (19). Molecular structures of N-methylimidazoles are present with the N₃ in blue. Error bars represent the standard deviations from at least three independent electrochemical measurements. The $^{14}$N₃/$^{15}$N₃ chemical shift changes were obtained by subtracting the resonance peak position in 10% CD₂Cl₂ + 90% CH₂Cl₂ from that in 0.1 M KOH with 10% D₂O + 90% H₂O (NMR spectra were given in Fig. S4).
In general, the N-methylimidazoles with more -CH$_3$(s) give higher $i_0$ improvements (Fig. 1; Table S1). No significant improvement was observed for imidazole that contains no -CH$_3$ (5±5%). As the number of -CH$_3$ increases, the $i_0$ improvement generally increases until reaching 57±2% for Me-N$_1$C$_2$ that contains two -CH$_3$(s). The position of -CH$_3$ also affects the improvement. The improvement of Me-N$_1$ (36±2%) with the -CH$_3$ bonded with N$_1$ is higher than those of Me-C$_4$ (14±3%) and Me-C$_2$ (28±4%). Similarly, the improvement of Me-N$_1$C$_2$ (57±2%) is higher than that of Me-C$_2$,$_4$ (33±2%). By contrast, 1,3-dimethyluracil with the two -CH$_3$(s) bonded with N$_1$ and N$_3$ does not improve the $i_0$ of Pt/C (Fig. S1B), which suggests that -CH$_3$ alone does not promote the HER/HOR of Pt/C.

To identify the promoting roles of -CH$_3$, DFT calculations were used to determine the partial charges of these N-methylimidazoles (19). We found that the $i_0$ improvement of these N-methylimidazoles increases monotonously with the negative charge of N$_3$ (Fig. 1), and the negative charge of N$_3$ is affected by the number and position of -CH$_3$ (Table S2), a well-known electron-donating group. These results suggest that the -CH$_3$(s) affect the N-methylimidazoles-induced HER/HOR activity improvement of Pt through tuning the charge of N$_3$.

To elucidate the catalytic role of N$_3$, we conducted $^{14}$N and $^{15}$N NMR experiments on these N-methylimidazoles in 0.1 M KOH as well as in CH$_2$Cl$_2$ solution as a baseline because the N atoms in N-methylimidazoles have minimal interactions with CH$_2$Cl$_2$ (21). Imidazole (Fig. S4A) and Me-C$_2$ (Fig. S4B) exhibit a single resonance in CH$_2$Cl$_2$ solution despite the co-presence of N$_1$ and N$_3$. The same phenomenon was previously observed on imidazole (21) and ascribed to the self-association via hydrogen-bonding (N$_3$ of a given imidazole binding with H$_1$ of a neighboring imidazole forming N$_3$···H$_1$ bond as illustrated in Fig. S4A, inset), which makes the N$_1$ and N$_3$ in these compounds with a symmetric ring structure equivalent. They also exhibit...
a single resonance in 0.1 M KOH (Fig. S4A) because of the rapid averaging of N1 and N3 charge via proton exchange (21). By contrast, Me-N1 (Fig. S4D) and Me-N1C2 (Fig. S4E) exhibit two separate resonances for N1 and N3, because the N1-CH3 bonding prevents the self-association and proton exchange (21). Me-C4 and Me-C2,4 also exhibit two resonance peaks but much closer to each other in both solutions (Fig. S4G-H). This is because they are subject to self-association and rapid proton exchange, but their asymmetric ring structure makes the N1 and N3 not identical. Therefore, the six N-methylimidazoles can be divided into three groups, and the only difference between the two N-methylimidazoles in each group is an additional -CH3 bonded with C2.

In CH2Cl2, the chemical shift of N3 is 265.3 ppm for Me-N1, whereas it is shifted upfield to 262.2 ppm for Me-N1C2 (Fig. S4D-E). This can be rationalized as the electron-donating -CH3 shields the nucleus by increasing its electron density and shifts the resonance peak upfield. This result agrees with the DFT calculation that the N3 of Me-N1C2 is more negative than that of Me-N1 (Table S2). When transferring from 0.1 M KOH to CH2Cl2 solution, the 14N3 chemical shift of Me-N1 and Me-N1C2 exhibits a downfield shift of 15.4 and 16.1 ppm, respectively. The change of the chemical shift of the 15N3 resonance (15.6 ppm) of Me-N1 (Fig. S4F) is extremely close to that of the 14N3 resonance. A comparable change of the 15N3 chemical shift (15 ppm) was previously reported by transferring Me-N1 from 0.1 M KOH to CH2Cl2 and ascribed to the change of the bonding from N3···H2O to N3 (21). This change thus verifies the interaction between the lone-pair electrons of the N3 and the H of the water (N3···H2O bond), which has been widely observed in N-methylimidazole solvent (22). Collectively, Me-N1C2 exhibits a more negative N3, stronger N3···H2O bond as reflected by a larger chemical shift change of N3 resonance, and higher i0 improvement than Me-N1 (Fig. 1). The same trends are also observed between imidazole and Me-C2 and between Me-C4 and Me-C2,4 (Fig. 1; Table S1-3). The trends
identified for all three groups indicate that the -CH₃(s) in these N-methylimidazoles tune the negative charge of N₃ and in turn the N₃···H₂O bond strength, thereby modulating the \( i_0 \) improvement. We infer from these results that these N-methylimidazoles promote the HER/HOR of Pt in 0.1 M KOH by binding the H₂O through the N₃···H₂O bond.

In situ ATR-SEIRAS was then conducted to probe the effects of N-methylimidazoles on the interfacial water structure near Pt surfaces during the HER/HOR (19). Spectra were collected during potential steps in an H₂-saturated 0.1 M KOH solution with and without \( 10^{-5} \) M Me-N_{1}C_{2}. For both cases, the spectra collected at 0.5 V (double-layer region) were used as a baseline for subtraction. The characteristic features of interfacial water, two \( \nu(\text{OH}) \) bands at ~3,500 and ~3,000 cm\(^{-1} \) (Fig. 2A) and a \( \delta(\text{HOH}) \) band at ~1,610 cm\(^{-1} \) (Fig. S5A) (23-25), are observed in the spectra collected in 0.1 M KOH free of Me-N_{1}C_{2} within the H\text{upd} potential region. It has been well established that water monomers (that is, without hydrogen bonding) possess \( \nu(\text{OH}) \) bands around 3,700 cm\(^{-1} \), and the hydrogen bonding among water molecules red-shifts and broadens the \( \nu(\text{OH}) \) bands substantially for hydrogen donors but modestly for hydrogen acceptors (23, 24, 26). Therefore, the broad band around 3,000 cm\(^{-1} \) is characteristic of the strongly hydrogen-bonded water structure composed of hydrogen donors (\( \uparrow \)H₂O, hydrogen-up orientation) in the first water layer next to the Pt surface; whereas the sharp band around 3,500 cm\(^{-1} \) arises from the weakly hydrogen-bonded water structure made of hydrogen acceptors (\( \downarrow \)H₂O, hydrogen-down orientation) in the first layer (23). Consistent with previous studies (23, 25), the intensity of the \( \nu(\text{OH}) \) band around 3,000 cm\(^{-1} \) progressively decreases as the potential reduces from 0.5 V to 0 V, accompanied by a slight growth of the \( \nu(\text{OH}) \) band between 3,300-3,500 cm\(^{-1} \), and both bands blue-shift (Fig. 2A). These spectral changes have been ascribed to the potential-dependent reorientation of \( \uparrow \)H₂O towards \( \downarrow \)H₂O with decreasing potential (23, 24). This potential-dependent
reorientation of interfacial water has also been observed by in situ Raman (27) and in situ X-ray diffraction (28), and rationalized by computations that Pt surfaces become more negatively charged with reducing potential (vs. RHE) and thus favor bonding with $\downarrow$H$_2$O over $\uparrow$H$_2$O (29).

Fig. 2. In situ probe of interfacial water and N-dimethylimidazoles. In situ ATR-SEIRAS spectra of the interfacial water on a Pt film collected in 0.1 M KOH (A) without and (B) with $10^{-5}$ M Me-N$_1$C$_2$. (C) In situ ATR-SEIRAS spectra of Me-N$_1$C$_2$ collected in 0.1 M KOH at 0 V with increasing concentration. (D) In situ ATR-SEIRAS spectra of Me-N$_1$C$_2$ with a concentration of $10^{-5}$ M in 0.1 M KOH at various potentials. In situ Raman spectra were collected in 0.1 M KOH
with 1 M (E) Me-N<sub>1</sub> and (F) Me-N<sub>1</sub>C<sub>2</sub> on an Ag electrode, with the derived orientations of these compounds depicted aside.

The general trends of the \( \nu(\text{OH}) \) bands are dramatically altered upon addition of \( 10^{-5} \) M Me-N<sub>1</sub>C<sub>2</sub> into 0.1 M KOH. The 3,000 cm\(^{-1}\) band undergoes neither decrease in intensity nor blue-shift with reducing potential (Fig. 2B), reflecting preservation of interfacial \( \uparrow \text{H}_2\text{O} \) structures. The drastic contrast in the trends of the \( \nu(\text{OH}) \) bands with or without Me-N<sub>1</sub>C<sub>2</sub> shows that Me-N<sub>1</sub>C<sub>2</sub> effectively suppresses the potential-dependent reorientation of interfacial water. This finding, together with the NMR and computational results, leads us to infer that N-methylimidazoles stabilize interfacial \( \uparrow \text{H}_2\text{O} \) through the N\(_3\)\( \cdots \)\( \uparrow \text{H}_2\text{O} \) bonding.

The negatively charged N\(_3\) of N-methylimidazoles needs to be located close to the negatively charged Pt surface to stabilize interfacial \( \uparrow \text{H}_2\text{O}. \) This paradox drives us to probe the adsorption mode of N-methylimidazoles within the interface. The peak at 1,440 cm\(^{-1}\), which was identified as the C-H bending mode of the -CH\(_3\) (30), gradually grows upon the addition of Me-N<sub>1</sub>C<sub>2</sub> into 0.1 M KOH when holding at 0 V (Fig. 2C). This observation indicates that the Me-N<sub>1</sub>C<sub>2</sub> is orientated with the -CH\(_3\)(s) facing towards the Pt surface at 0 V, in agreement with previous DFT calculations (31). However, the lack of shift of this peak with changing potential (Fig. 2D) indicates the lack of stark effects and thus the lack of strong covalent interactions (or specific adsorption) between Me-N<sub>1</sub>C<sub>2</sub> and the Pt surface (32). This is further confirmed by X-ray absorption spectroscopy (XAS) from the Pt perspective. The XAS spectrum at the Pt L\(_3\)-edge remains unchanged upon adding Me-N<sub>1</sub>C<sub>2</sub> onto a Pt electrode (Fig. S6), which excludes specific adsorption of Me-N<sub>1</sub>C<sub>2</sub> on Pt/C given that specific adsorption of H (33) on Pt/C change the Pt L\(_3\)-edge XAS spectrum markedly. The non-specific adsorption (or non-covalent interaction) of
N-dimethylimidazoles on Pt surfaces is in line with the electrochemical results that adding $10^{-5}$ M N-methylimidazoles in 0.1 M KOH does not reduce the HOR limiting current (Fig. S2). The non-specific adsorption of Me-N$_1$C$_2$ on Pt/C rules out the possibility that Me-N$_1$C$_2$ reorients interfacial water through Pt by modifying its electronic properties.

In situ Raman was implemented to probe the orientation of N-methylimidazoles near the silver (Ag) electrode in 0.1 M KOH (19), given that the feasibility of this method was demonstrated previously thanks to the enhancement effect of Ag on Raman signals (34). The dynamic orientation of N-methylimidazoles on Ag surfaces shall be applicable to Pt surfaces since they are non-specifically adsorbed on metal surfaces and their orientation is dictated by the interfacial IEF. The in situ Raman spectra of Me-N$_1$ exhibit two sets of dynamic peaks within 2,800-3,200 cm$^{-1}$ in the potential range of -0.4-0.1 V (Fig. S7A), matching well with those of Me-N$_1$ previously reported in 0.1 M KCl (34). Most importantly, the growth and broadening of the $\nu$(CH$_3$) bands between 2,850-2,950 cm$^{-1}$ with reducing potential observed here (Fig. 2E) and previously (34) reflects the potential dependent orientation of Me-N$_1$. In principle, the interfacial Me-N$_1$ interacts with the positively charged surface through the N$_3$ lone pair electrons, placing the -CH$_3$ bonded with C$_1$ pointing away from the surface (N$_3$-bound mode); whereas it interacts with the negatively charged surface preferentially through the -CH$_3$ (-CH$_3$-bound mode) (Fig. 2E, inset) (31, 34). Therefore, as the surface becomes increasingly negatively charged with reducing potential (34), the interfacial Me-N$_1$ reorientates from the N$_3$-bound mode to -CH$_3$-bound mode, resulting in the growth of the $\nu$(CH$_3$) bands. By contrast, the $\nu$(CH$_3$) bands of Me-N$_1$C$_2$ are largely preserved within the potential range of -0.4-0.1 V (Fig. 2F). The same phenomenon was previously observed on Me-C$_2$ and explained as the -CH$_3$ is bonded with the C$_2$ next to N$_3$, so it remains close to the surface even though the surface interacts with N$_3$ (34). This geometry
certainly applies for Me-N1C2 (Fig. 2F, inset). These in situ Raman results indicate that the -CH3(s) hold N-methylimidazoles close to the negatively charged surface, thereby placing the N3 close to the surface to interact with interfacial water. Collectively, the -CH3(s) of N-methylimidazoles play a dual role in promoting the HER/HOR of Pt: tuning the negative charge of N3 and holding it close to the negatively charged surface. Neither imidazole with N3 but lack of -CH3 nor 1,3-dimethyluracil with -CH3(s) but lack of unoccupied N3 promotes the HER/HOR of Pt in 0.1 M KOH.

Next, we explain why stabilizing the ↑H2O facilitates the HER/HOR of Pt in base from the reaction kinetics perspective. The Volmer step Had + OH- ↔ H2O + e-, a typical PCET process (35, 36), has been acknowledged as the rate-determining step (rds) of the HER/HOR of Pt in base. We previously proposed that interfacial water shuffles the HER/HOR intermediates through the interface during the Volmer step (17). Here we refine this mechanism by adopting the Grothuss mechanism to account for the diffusion of proton (37) and hydroxide (38) through the H-bond network of water. An H2O dimer, which is composed of one hydrogen acceptor (↓H2O) and one hydrogen donor (↑H2O), is chosen as the smallest unit to represent the H-bond network of water. Its presence on Pt surfaces under vacuum was observed experimentally (39, 40), and on Pt and Au surfaces under bias voltage was supported by density functional theory (DFT) calculations (41) and in situ Raman (27). An H2O dimer approaches the Pt surface to trigger the PCET (Fig. 3A, (i) → (ii)) as recently proposed by Hammes-Schiffer’s group (35). This step was simulated by the DFT (42) that showed the Pt-H bond length decreases abruptly from ~2.3 Å to ~1.6 Å as the Volmer step occurs. Upon specific adsorption of the dimer, the ↓H2Oad donates one proton to the Pt surface and meanwhile accepts a proton from the ↑H2Oad (Fig. 3A, (ii) → (iii)), which is coupled with the circulation of an electron from the Pt surface to
the $\downarrow \text{H}_2\text{O}_{\text{ad}}$, $\uparrow \text{H}_2\text{O}_{\text{ad}}$, and then back to the Pt surface as indicated by yellow arrows in Fig. 3A, (ii) (35, 4I). The overall process results in the formation of a specifically adsorbed hydrogen (H$_{\text{ad}}$, blue) and hydroxyl (OH$_{\text{ad}}$, red) on adjacent Pt atoms and an H$_2$O molecule in the outer Helmholtz plane (OHP): 2Pt + $\text{H}_2\text{O}$···$\text{H}_2\text{O}$ $\rightarrow$ Pt-$\text{H}_{\text{ad}}$···OH$_2$···OH$_{\text{ad}}$-Pt (Fig. 3A, (iii)). This step is spontaneously followed by the transfer of an electron from the Pt to the OH$_{\text{ad}}$ and then to the H$_2$O molecule, coupled with the back donation of a proton from the H$_2$O to the OH$_{\text{ad}}$: Pt-$\text{H}_{\text{ad}}$···OH$_2$···OH$_{\text{ad}}$-Pt + e$^-$ $\rightarrow$ Pt-$\text{H}_{\text{ad}}$ + OH$^-$···$\uparrow \text{H}_2\text{O}_{\text{ad}}$-Pt (Fig. 3A, (iii) $\rightarrow$ (iv)). This step is equivalent to the transport of the OH$_{\text{ad}}$ to the OHP in the form of OH$^-$ via the Grotthuss mechanism. The $\uparrow \text{H}_2\text{O}_{\text{ad}}$···OH$^-$ then moves away from the Pt surface (Fig. 3A, (iv) $\rightarrow$ (v)) by the repelling IEF and decreased electronic coupling between the $\uparrow \text{H}_2\text{O}_{\text{ad}}$ and Pt surfaces (36, 42).

The reverse direction (Fig. 3A, (v) $\rightarrow$ (i)) describes the Volmer step of the HOR of Pt in alkaline solution. The net results of the two consecutive processes (Fig. 3A, (ii) $\leftrightarrow$ (iv)) are equivalent to the dissociation/formation of the $\downarrow \text{H}_2\text{O}_{\text{ad}}$ via PCET (Fig. 3A, (vi)), which leads to an apparent pathway of (i) $\leftrightarrow$ (vi) $\leftrightarrow$ (v) without explicitly involving OH$_{\text{ad}}$ as proposed by Tang’s and Snyder’s groups (43, 44). The $\uparrow \text{H}_2\text{O}_{\text{ad}}$ is not consumed along the apparent pathway, and therefore serves as a catalyst promoting the Volmer step by enabling the diffusion of OH$^-$ via the Grotthuss mechanism. A similar pathway is proposed for terrace surfaces such as Pt(111) that do not specifically bind oxygen species ($\uparrow \text{H}_2\text{O}$ and OH$^-$) within the $\text{H}_{\text{upd}}$ potential region (Fig. 3B) (45, 46). For this case, the $\uparrow \text{H}_2\text{O}$ is quasispecifically adsorbed ($\uparrow \text{H}_2\text{O}_{\text{qad}}$) (47) through the H$_{\text{ad}}$ to catalyze the PCET. The proposed reaction mechanism also applies for acidic solution (Fig. S8), in which interfacial water transfers proton via the Grotthuss mechanism (37). Therefore, the HER/HOR kinetics of Pt in aqueous solution is unified by diffusion of proton (acid) or hydroxide (base) through the interface by interfacial water via the Grotthuss mechanism.
Fig. 3. Proposed mechanisms for the Volmer process on Pt surfaces. The elementary steps of the Volmer process of (A) stepped Pt surfaces and (B) terrace Pt surfaces in base. In (B), the water molecule in purple quasispecifically adsorbs onto Pt surfaces and triggers the PCET to donate a proton (blue) to the Pt surface coupled with an electron donation from the Pt surface, which is accompanied by the transfer of a proton from neighboring water, leading to the formation of an \( \uparrow \text{H}_2\text{O}_{\text{quad}} \) (in the dashed circle) through a \( \text{H}_{\text{ad}} \) (blue) and a hydroxide (red) in OHP. (C) Me-N₁C₂ stabilizes \( \uparrow \text{H}_2\text{O}_{\text{ad}} \) on the stepped Pt surface, (D) Me-N₁C₂ stabilizes \( \uparrow \text{H}_2\text{O}_{\text{quad}} \) on the terrace Pt surface, and (E) surface Ru stabilizes \( \uparrow \text{H}_2\text{O}_{\text{ad}} \). The orange arrows represent the
direction of electron transfer. Solid and dashed lines represent the covalent and non-covalent bonds, respectively, as defined in Ref(45). The different number of dashes indicates different bond lengths.

Because of the high polarity of water, the orientation of interfacial $\uparrow$H$_2$O depends strongly on the IEF, and in turn the pH since the IEF shifts with pH (48). As the pH increases, the pzfc shifts positively towards higher potential (vs RHE), making the Pt surface increasingly negatively charged and the IEF stronger (12, 48). Consequently, the interfacial $\uparrow$H$_2$O is increasingly destabilized and reorientated by the repelling IEF with increasing pH, as recently shown by Goddard’s group (49) using quantum mechanical calculations. They found that the number of interfacial $\uparrow$H$_2$O on Pt(100) is reduced by a factor of 3 as the pH increases from 0.2 to 12.8 (49). The $\uparrow$H$_2$O is required by our mechanism to catalyze the PCET, and thus destabilization or reorientation of it by the IEF accounts for the slow HER/HOR kinetics of Pt at high pH. N-methylimidazoles promote the HER/HOR of Pt surfaces by stabilizing the $\uparrow$H$_2$O.

Likewise, Ru promotes the HER/HOR of Pt by stabilizing the $\uparrow$H$_2$O$_{ad}$ via bonding with its O (Fig. 3E) as we recently proposed (17). Experimental observations of the $\uparrow$H$_2$O$_{ad}$ and OH$_{ad}$ on the Ru deposited on Pt surfaces during the HER/HOR in alkaline solution (6, 17) indicate that Ru sufficiently stabilizes the $\uparrow$H$_2$O$_{ad}$ against the repelling IEF, and consequently the rds shifts to the removal of OH$_{ad}$ (Fig. 3A, (iii) → (iv) for HER and (iii) → (ii) for HOR) as recently proposed by McCrum and Koper (4). The high oxophilicity of Ru combined with the observation of OH$_{ad}$ on Ru during the HER/HOR led to the proposition of the bifunctional mechanism, by which Ru promotes the HER/HOR of Pt by facilitating water dissociation and hydroxide adsorption, respectively (4, 6, 7). However, adding $10^{-5}$ M N-methylimidazoles into 0.1 M KOH
substantially delays the CO oxidation on Pt/C (Fig. S9). The same phenomenon was also observed for caffeine (18). This phenomenon indicates that N-methylimidazoles inhibit rather than facilitate hydroxide adsorption like Ru (6). Therefore, the bifunctional mechanism cannot account for the promoting roles of N-methylimidazoles. Another hypothesis that Ru promotes the HER/HOR of Pt by modifying its inherent properties via strain and/or electronic effects is inapplicable to N-methylimidazoles as they are non-specifically adsorbed on Pt surfaces. By our mechanism, the promoting roles of Ru and N-methylimidazoles on the HER/HOR of Pt in base can be unified to the stabilization of interfacial $\uparrow \text{H}_2\text{O}$ by binding with its O from below (Fig. 3E) and with its H from above (Fig. 3C-D), respectively.

Stabilization of interfacial $\uparrow \text{H}_2\text{O}$ also promotes the HER/HOR kinetics of Pt in practical devices with alkaline media such as anion exchange membrane electrolyzers (AEMELs), for which the repelling interfacial IEF is expected from the high pH environment. By adding $10^{-5}$ M Me-\text{N}_1\text{C}_2 into the 0.1 M KOH solution fed into the Pt/C cathode of an AEMEL (19), the $iR$-corrected current density at 1.6 V increased by ~40% (Fig. 4). This result demonstrates a new route to improve the AEMEL performance by introducing organic compounds into the interface to stabilize interfacial $\uparrow \text{H}_2\text{O}$. 
Fig. 4. Me-N₁C₂ improves the AEMEL performance. AEMEL polarization curves with and without adding $10^{-5}$ M Me-N₁C₂ into the 0.1 M KOH solution fed into the cathode with and without iR-correction. Cathode: 0.12 mgPt·cm⁻² Pt/C; anode: 3.1 mgIrOₓ·cm⁻² IrOₓ; membrane: PAP-TP-85-MQN-10C; 60 °C; electrode area 25 cm².

REFERENCES AND NOTES


19. See supplementary materials.


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**COMPETING INTERESTS**

The authors declare no competing financial interests.

**SUPPLEMENTARY MATERIALS**

Materials and Methods

Tables S1 - S3

Fig S1 - S9
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